

(19) Patent Office, Japanese Government (JP)

(12) Laid Open Patent Gazette (A)

(11) Laid Open Patent Publication No.

Hei 8 / 1996- 165210

(43) Date of Laid Open Publication:

June 25, 1996

(51) Int. Cl. ⁵	ID Symbol	Office File No.	FI	Technology Indication	Location
----------------------------	-----------	-----------------	----	-----------------------	----------

A 01 N 59 / 18					
----------------	--	--	--	--	--

	A				
--	---	--	--	--	--

	Z				
--	---	--	--	--	--

25 / 10					
---------	--	--	--	--	--

59 / 20					
---------	--	--	--	--	--

Request for examination: yet to be submitted

No. of Claims : 3 FD (6 pages in all)

(21) Application No. Hei 6 / 1994- 333532

(22) Date of Application : December 14, 1994



(71) Applicant: 00203656

Taki Kagaku Kogyo K. K, Co., LTD (Taki Chemical Co., Ltd.).

2, Midori – machi, Beppu –cho, Kakogawa City, Hyougo Prefecture

(71) Applicant: 000131245

Seed K. K, Co., Ltd. (Seed Co., Ltd.)

40 – 2, Hongo, 2 – chome, Bunkyo – ku, Tokyo

(72) Inventor : Kenji Uno

c / o Seed K. K, Co., Ltd. (Seed Co., Ltd.)

40 – 2, Hongo, 2 – chome, Bunkyo – ku, Tokyo

(72) Inventor : Hironobu Fukuzaki

1 – 16 – 4, Ninomiya, Tsukuba City, Ibaraki Prefecture

(72) Inventor : Yukari Imamura

4 – 2- 22, Higashi Konjuku, Himeji City, Hyogo Prefecture

continued to the last page

(54) [Title of the Invention] A Process for the Production of
Antimicrobial Agent and an Antimicrobial Agent

[57] [Abstract]

[Purpose]

To obtain an antimicrobial agent consisting of polymer particles containing an antimicrobial metal whose antimicrobial and antifungal effects are improved in terms of the lasting performance.

[Constitution]

To obtain an antimicrobial agent containing an antimicrobial metal characterized in that in copolymerizing raw materials for polymerization, (1) an ester of acrylic acid or an ester of methacrylic acid, and / or (2) an ester of di- or tri- acrylic acid or an ester of di- or tri- acrylic acid and (3) a radical polymerizing raw material having a sulfonic acid group / groups, an aqueous solution that contains silver ions, copper ions or zinc ions is added in the presence of an organic solvent and then (1) and / or (2) and (3) are allowed to undergo copolymerization.

[What we claim is]

[Claim 1]

A process for the production of an antimicrobial agent containing an antimicrobial metal characterized in that in copolymerizing raw materials

for polymerization, (1) an ester of acrylic acid or an ester of methacrylic acid, and / or (2) an ester of di- or tri- acrylic acid or an ester of di- or tri- methacrylic acid and (3) a radical polymerizing raw material having a sulfonic acid group / groups, an aqueous solution that contains silver ions, copper ions or zinc ions is added in the presence of an organic solvent and then (1) and / or (2) and (3) are allowed to undergo copolymerization.

[Claim 2]

A process for the production, in accordance with Claim 1, characterized in that the organic solvent is ethyl acetate, ethyl propionate, ethyl – n- hexanate, hexane, benzene, methyl iso- butyl ketone, methyl ethyl ketone, acetone, toluene, xylene.

[Claim 3]

An antimicrobial agent characterized in that in copolymerizing raw materials for polymerization, (1) an ester of acrylic acid or an ester of methacrylic acid, and / or (2) an ester of di- or tri- acrylic acid or an ester of di- or tri- methacrylic acid and (3) a radical polymerizing raw material

having a sulfonic acid group / groups, an aqueous solution that contains silver ions, copper ions or zinc ions is added in the presence of an organic solvent, followed by copolymerization.

[Detailed Explanation of the Invention]

[0001]

[Utilization Field in the Industry]

The present invention relates to a process for the production of an antimicrobial agent consisting of polymer particles containing an antimicrobial metal whose antimicrobial and antifungal effects are improved in terms of the lasting performance.

[0002]

[Conventional Technology]

For some years there have been known in the art that a minute amount of metal ions such as silver, copper and zinc can provide an antimicrobial and antifungal effects, and such antimicrobial metal ions are added to an insecticide, a disinfectant, etc. in a form of a metal salt such as silver

nitrate, and have been widely used in various fields. However, since such a metal salt is handled in a state of an aqueous solution, the use thereof is limited, and in addition in the case of silver nitrate, it has a strong mucous irritating action on the human body and there are many safety issues.

[0003]

In view of these circumstances, there have been attempts and studies in recent years to improve the long lasting properties of the antimicrobial activities as well as the ease of handling by allowing antimicrobial metal ions such as silver ions to be carried on various types of carriers. For example, there have been disclosed examples in which as such a carrier, use is made of activated carbon (Japanese Patent Gazette, Patent Publication No. Sho 52 / 1977), non – crystalline alumino silicate (Japanese Laid Open Patent Gazette, Laid Open Patent Publication No. Hei 3 / 1991 – 23960), etc., and there various types of carriers are allowed to carry antimicrobial metal ions. However, since these carriers are all inorganic compound ones, the dispersibility in a resin, a coating,

etc. based on substrate materials made of an organic polymer is poor, and thus their uses are limited.

[0004]

Therefore, development of an antimicrobial agent with a substrate of an organic polymer has been hoped for as an antimicrobial agent that can be used for an organic polymer resin, and various antimicrobial agents have been investigated and studied. For example, there has been disclosed a method (Japanese Laid Open Patent Gazette, Laid Open Patent Publication No. Hei 3 / 1991 – 141205) in which an antimicrobial metal ions are used in a form of a salt of a surface active agent, however since such an antimicrobial agent is such that antimicrobial metal ions are carried simply as a salt of a surface active agent, there is problem in that metal ions are easily eluted.

[0005]

In view of such circumstances, one of the applicants of the present invention studied a method by which to allow antimicrobial metal ions to be carried on organic polymer particles, and has disclosed an

antimicrobial agent having a long lasting antimicrobial activities and a process for the production thereof (Japanese Laid Open Patent Gazette, Laid Open Patent Publication No. Hei 4 / 1992 – 173712). With this antimicrobial agent, since the carrier is an organic polymer, the compatibility with other polymer resins is superior. This technology is the one in which an antimicrobial agent is produced by obtaining a carrier polymer by the emulsion polymerization with water as a dispersion medium and then by mixing and allowing antimicrobial metal ions to react with it. As a result of further repeated studies on this method, it has become clear that with this antimicrobial agent antimicrobial metal is distributed on the surface of the carrier, the antimicrobial metal tends to be separated easily, resulting in faster elution rate, and thus the long lasting properties of the antimicrobial effects is not sufficient. Furthermore, it has been made clear that since the method of allowing an antimicrobial metal to be carried on a polymer obtained by the emulsion polymerization in an aqueous solution requires the use of a large, excess amount of a metal salt, the carrying efficiency is poor, it is not

economical in terms of yield when using silver ions, which are expensive.

Therefore, the current situation is such that no antimicrobial agent with an excellent long lasting property of antimicrobial activities that can be mixed uniformly with various types of polymers, has not been obtained.

[0006]

[Problem Points which the Invention Tries to Solve]

The inventors of the present invention studied a method by which to obtain an antimicrobial agent that is excellent in compatibility with various types of polymers and in long lasting property of antimicrobial activities and further studied a method by which to allow an antimicrobial metal to be carried on the above - mentioned organic polymer particles.

And furthermore, the inventors of the present invention have made extensive studies on a method by which to allow an antimicrobial metal to be uniformly and strongly bound to in a polymer carrier, thereby improving the long lasting property of antimicrobial activities, and to solve the problem point in terms of yield that becomes an issue in a case in which an expensive metal such as silver is used.

[0007]

As a result, the inventors of the present invention have found that polymer particles containing an antimicrobial metal obtained by adding an aqueous solution containing antimicrobial metal such ions as silver ions in advance in the presence of an organic solvent and by allowing a raw material, an ester of acrylic acid, and another raw material of a radical polymerizability having a sulfonic acid group / groups to undergo copolymerization, become an excellent antimicrobial agent that is capable of solving the above - mentioned problems, and have achieved the present invention based on this finding.

[0008]

[Means by which to Solve the Problem Points]

That is, the present invention relates to a process for the production of an antimicrobial agent containing an antimicrobial metal characterized in that in copolymerizing raw materials for polymerization, (1) an ester of acrylic acid or an ester of methacrylic acid, and / or (2) an ester of di- or tri- acrylic acid or an ester of di- or tri- methacrylic acid and (3) a radical

polymerizing raw material having a sulfonic acid group / groups, an aqueous solution that contains silver ions, copper ions or zinc ions is added in the presence of an organic solvent and then (1) and / or (2) and (3) are allowed to undergo copolymerization, and furthermore relates to an antimicrobial agent that can be obtained by such a process for the production.

[0009]

[Action]

In the following, we shall explain the present invention in more detail.

The antimicrobial agent in accordance with the present invention is obtained by using raw materials for polymerization, (1) an ester of acrylic acid or an ester of methacrylic acid, and / or (2) an ester of di- or tri-acrylic acid or an ester of di- or tri- methacrylic acid and (3) a radical polymerizing raw material having a sulfonic acid group / groups, and by copolymerizing these raw materials, and the important point in doing so is that an aqueous solution of a salt of such an antimicrobial metal is added to a solution obtained by dissolving or dispersing these raw

materials in an organic solvent in advance and then copolymerization is allowed to take place. By carrying out these operations, the sulfonic acid groups in the raw material (3) for polymerization become a salt of an antimicrobial metal, and an antimicrobial agent in which the antimicrobial metal is uniformly distributed and bound in the polymer particles can be obtained by the copolymerization reaction.

[0010]

Now let us explain in more detail the raw materials for polymerization to be used in the present invention. As examples of the raw material for polymerization (1): an ester of acrylic acid or an ester of methacrylic acid, mention may be made of, for example, various types of esters of acrylic acid or esters of methacrylic acid of aliphatic alcohols such as methyl acrylate, ethyl acrylate, butyl acrylate, 2 – ethyl hexyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, octyl acrylate, and octyl methacrylate, and various types of esters of acrylic acid or esters of methacrylic acid of alicyclic alcohols such as cyclo - hexyl acrylate, cyclo – hexyl methacrylate, cyclo – hexyl methyl acrylate, and cyclo – hexyl

methyl methacrylate. Furthermore, mention may be made of various types of esters of acrylic acid or esters of methacrylic acid of aromatic alcohols such as phenyl acrylate, phenyl methacrylate, benzyl acrylate and benzyl methacrylate. In addition, mention may be made of various types of esters of acrylic acid or esters of methacrylic acid containing a hydroxyl group / groups such as 2 – hydroxy ethyl acrylate, and 2 – hydroxy ethyl methacrylate, or various types of esters of acrylic acid or esters of methacrylic acid containing a halogen / halogens such as 4-bromo – phenyl acrylate and 4 – bromo – phenyl methacrylate. However, it should be understood that they are not limited only to those mentioned above.

[0011]

Next, as examples of the raw materials for polymerization (2) esters of di- or tri- acrylic acid or esters of di- or tri- methacrylic acid, use can be made of esters of bifunctional di- acrylic acid or esters of bifunctional di-methacrylic acid such as ethylene glycol di- acrylate, ethylene glycol di-methacrylate, propylene di- acrylate, propylene di- methacrylate, di –

ethylene glycol di- acrylate, di- ethylene glycol di- methacrylate, poly ethylene glycol di- acrylate, poly ethylene glycol di- methacrylate, 1, 3- di- acryloxy – 2 – propanol, and 1, 3 – di- methacryloxy propanol, esters of tri- functional acrylic acid or esters of tri- functional methacrylic acid such as such as tri- acrylate of glycerine, tri- methacrylate of glycerine, tri- acrylate of tri- methylol propane or tri- methacrylate of tri- methylol propane, etc. However, it should be understood that they are not limited only to those mentioned above.

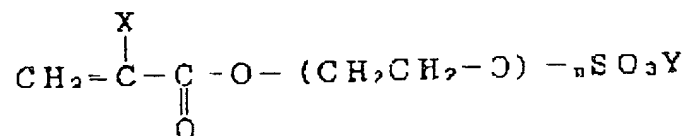
[0012]

Next, as the raw materials for polymerization (3) : a radical polymerizing raw material having a sulfonic acid group / groups, mention may be made of

[0013]

a compound having a radical polymerizing acryl group / groups or a methacryl group / groups, having the chemical structure expressed by the following chemical formula [1]

[Chemical Formula 1]

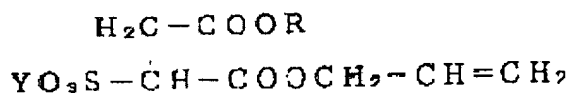


(where $n \geq 6$, X is either H or CH₃, and Y is either H or Na, K or NH₄)

or a compound having the chemical structure expressed by the following chemical formula [2], having an allyl group / groups and a sulfonic acid group / groups

[0014]

[chemical formula 2]



(where R is an alkyl group, a phenyl group and a benzyl group, and Y is either H or Na, K and NH₄).

[0015]

Furthermore, it is possible to use a compound having a radical polymerizing double bond / bonds and a sulfonic acid group / groups such as a compound obtained by adding ethylene oxide and propylene oxide to nonyl phenol having an allyl group / groups and carrying out

sulfuric acid esterification.

[0016]

In addition to such raw materials for polymerization (1) and / or (2) and (3), it is possible to utilize other monomers that can be copolymerized to these raw materials for polymerization in the present invention. Such a monomer is useful in order to increase the compatibility with a resin in a case in which the antimicrobial agent in accordance with the present invention is mixed with other resin. As an example of such a monomer, use can be made of styrene, di- vinyl benzene, di- allyl phthalate, tri- acryl cyanurate, vinyl chloride, vinyl acetate, acrylnitrile, α - methyl styrene, butadiene, etc. depending on purposes.

[0017]

In the present invention, first these raw materials for polymerization (1) and / or (2) and (3) are dissolved or dispersed in an organic solvent. As for the types of such organic solvents, use can be made of ethyl acetate, ethyl propionate, ethyl - n- hexanate, hexane, methyl iso- butyl ketone, methyl ethyl ketone, acetone, benzene, toluene, xylene, etc. However, in

a case in which use is made of water in place of such organic solvents, it is impossible to obtain an antimicrobial agent, which is the target of the present invention.

[0018]

Furthermore, an aqueous solution that contains silver ions, copper ions or zinc ions are added to this organic solvent in advance. Such as aqueous solution of antimicrobial metal ions is obtained by dissolving in a small quantity of water a metal salt of silver nitrate, copper sulfate, copper nitrate, copper acetate, zinc nitrate, zinc acetate, etc. The important point of the present invention is to carry out the polymerization reaction in the presence of such an organic solvent, and by this, the sulfonic acid groups bound to metal ions are allowed to uniformly be distributed in a polymer carrier. Therefore, in a case in which use is made of water in place of an organic solvent, this reaction becomes an emulsion polymerization reaction, the sulfonic acid groups are distributed only on the surface of a polymer carrier, and thus since an antimicrobial metal is distributed only on the surface of a carrier, separation of an antimicrobial metal can

proceed easily, and it becomes difficult to maintain antimicrobial activities of an antimicrobial agent over a long period of time.

[0019]

The ratios of use of the raw materials for polymerization : (1) and / or (2) and (3) in the present invention with respect to the composition of the antimicrobial agent, which is the target of the present invention are as follows: that of an ester of acrylic acid or an ester of methacrylic acid (raw material (1)) is 0 to 95 % by wt, especially preferably 20 to 70 % by wt; that of an ester of di- or tri- acrylic acid or an ester of a di- or tri-methacrylic acid (raw material (2)) is 0 to 95 % by wt, especially preferably 20 to 70 % by wt, and that of a radical polymerizing raw material having a sulfonic acid group / groups (raw material (3)) is preferably 5 to 50 % by wt. Here with respect to the ratio of use of raw material (1) and raw material (2), in a case in which the antimicrobial agent requires to be soft, it is only necessary to increase mainly the amount of use of raw material (1), while in a case in which it is required to be hard, it is only necessary to increase the amount of raw material (2).

Furthermore, the amount of use of a radical polymerizing raw material having a sulfonic acid group / groups (raw material (3)) is in a proportional relation to the amount of an antimicrobial metal to be carried on a polymer carrier, and it is correlated to the desired antimicrobial activities of an antimicrobial agent to be used. And it is used in a quantity of 5 % by wt or higher, preferably 20 % by wt or higher with respect to the total quantity of the monomers of these raw materials. However, as to the upper limit thereof, 50 % by wt is set, and an amount above this is not preferable because the hydrophilic property of such an antimicrobial agent becomes too strong above this amount and it becomes difficult to maintain the antimicrobial activities for a long period of time. The amount of use of an organic solvent is preferably about 2 to 20 times in quantity with respect to the total amount of raw materials (1) and / or (2) and (3).

[0020]

The copolymerization reaction is carried out for about 2 to 10 hrs by adding a polymerization initiator to a solution of such raw materials, and

heating the reaction system to a temperature of 50 to 80 ° C under reflux , while stirring. As to such a polymerization initiator, use can be made of benzoyl peroxide, ammonium persulfate, potassium persulfate, etc. With the progress in polymerization, the antimicrobial agent in accordance with the present invention whose antimicrobial metal salt carried on a carrier is allowed to precipitate as particles of about 0.5 to 50 μ m in average particle diameter. After stopping the reaction, the copolymer particles precipitated are separated by filtering, etc., and if necessary, after washing with an organic solvent or water, they are dried and thus an antimicrobial agent in accordance with the present invention in a powder form can be obtained.

[0021]

[Examples Embodying the Invention]

In the following we shall explain the present invention by citing some examples embodying the invention. In these examples embodying the invention, % means % by wt unless otherwise noted.

[0022]

(Example 1)

Five hundred g of n- hexane was placed as an organic solvent in a 4-necked flask of a capacity of 1 L equipped with a stirrer, and 31.4 g of the radical polymerizing raw material having a sodium sulfonate group expressed by chemical formula 2 (made by Sanyo Kasei Kogyo Co., Ltd., Trade name JS – 2, 38 % aqueous solution), 42.5 g of methyl methacrylate, and 4.7 g of di- ethylene glycol di- methacrylate were added thereto, thereby dissolving them therein. Furthermore, 15.4 g of 30 % aqueous solution of silver nitrate and 0.5 g of benzoyl peroxide as a polymerization catalyst were added thereto. Next, the reaction system was heated to 50 °C under agitation while removing gas from the solution by nitrogen substitution, and the reaction was continued for 10 hrs. With the progress of the reaction, the copolymer was produced as a suspension of fine particles.

[0023]

The suspended particles were separated and taken out by suction filtration of the suspension after the reaction, and after washing them

with n – hexane, and vacuum drying of them resulted in 57 g of an antimicrobial agent in accordance with the present invention. The silver content in the antimicrobial agent obtained by measuring the antimicrobial agent in accordance with the present invention by the atomic absorption method was 3.7 %. In addition, this antimicrobial agent was dispersed in water by use of an ultrasonic agitator, and the particle diameters thereof were measured by the centrifugal precipitation method by use of a centrifugal precipitation type particle size distribution measuring device. The average particle diameter thus obtained was 3 μ m.

[0024]

(Example 2)

Without using the methyl methacrylate used in Example 1, use was made of 50 g of diethylene glycol di- methacrylate, a reaction was allowed to take place in a manner similar to Example 1, and 59 g of an antimicrobial agent in accordance with the present invention was obtained. The silver content of the antimicrobial agent measured was 3.6 %. And the average

particle diameter was 4 μ m.

[0025]

(Example 3 through Example 5)

Without using the methyl methacrylate used in Example 1, use was made of 50 g of diethylene glycol di- methacrylate, and furthermore use was made of ethyl acetate (Example 3), methyl iso- butyl ketone (Example 4) or xylene (Example 5) as an organic solvent in place of the n – hexane used in Example 1, a reaction was allowed to take place in a manner similar to Example 1, and antimicrobial agents in accordance with the present invention were obtained. The silver contents of the antimicrobial agents and the average particle diameters were measured and the results are given in Table 1.

[0026]

Table 1

	Amount obtained (g)	Silver content (%)	Average particle diameter (μ m)
Example 3	52	3.3	3
Example 4	58	3.9	2
Example 5	52	3.2	10

[0027]

(Example for comparison 1)

Without using the methyl methacrylate used in Example 1, use was made of 50 g of diethylene glycol di- methacrylate, and furthermore use was made of water as a solvent in place of the n – hexane used in Example 1, and 0.5 g of potassium persulfate in place of benzoyl peroxide, which was a catalyst, and a reaction was allowed to take place in a manner similar to Example 1. the average particle diameter of 40 g of an antimicrobial agent obtained was 0.4 μ m and the silver content of the antimicrobial agent was measured to be 0.13 %.

[0028]

(Example for Comparison 2)

Use was made of water in place of the n – hexane used in Example 1, and 0.2 g of potassium persulfate in place of benzoyl peroxide, which was a catalyst, and an emulsion polymerization reaction was carried out without adding an aqueous solution of silver nitrate. As a result, an emulsion polymer having an average particle diameter of 0.1 μ m. A precipitate was obtained by putting this emulsion polymer in a large amount of 10 % aqueous solution of silver nitrate and stirring it. By filtering, washing with water and freeze- drying it, 54 g of an antimicrobial agent having a silver content of 4.5 % was obtained.

[0029]

(Example 6)

Without using the methyl methacrylate used in Example 1, use was made of 50 g of diethylene glycol di- methacrylate, and furthermore use was made of ethyl acetate as a solvent and 25.0 g of the radical polymerizing raw material expressed by chemical formula 1, having a sulfonic acid

group (made by Sanyo Kasei Kogyo Co., Ltd., trade name RS – 30, 50 % aqueous solution), a reaction was allowed to take place in a manner similar to Example 1, and 57 g of an antimicrobial agent in accordance with the present invention was obtained. The silver content of the antimicrobial agent measured was 3.8 %. And the average particle diameter was 2 μ m.

[0030]

(Example 7)

Without using methyl methacrylate used in Example 1, use was made of 50 g of diethylene glycol di- methacrylate, and furthermore use was made of methyl iso- butyl ketone as an organic solvent and 13.6 g of 5- hydrate of copper sulfate (25 % aqueous solution) as an antimicrobial metal salt, and a reaction was allowed to take place in a manner similar to Example 1, and 50 g of an antimicrobial agent in accordance with the present invention was obtained. The copper content of the antimicrobial agent measured was 1.6 %. And the average particle diameter was 15 μ m.

[0031]

(Example 8)

Without using methyl methacrylate used in Example 1, use was made of 50 g of diethylene glycol di- methacrylate, and furthermore use was made of methyl iso- butyl ketone as an organic solvent and 15.6 g of 7- hydrate of zinc sulfate (25 % aqueous solution) as an antimicrobial metal salt, and a reaction was allowed to take place in a manner similar to Example 1, and 48 g of an antimicrobial agent in accordance with the present invention was obtained. The zinc content of the antimicrobial agent measured was 1.4 %. And the average particle diameter was 10 μ m.

[0032]

<Antimicrobial evaluation test 1>

By using the antimicrobial agents obtained in Example 1 through Example 8 and Example for Comparison 1, minimum inhibition concentrations for various test microorganisms (MIC) were measured, and the antimicrobial performance of the antimicrobial agents was evaluated. As test microorganisms, use was made of Escherichia coli (IFO – 3301) (E. coli), Pseudomonas aeruginosa (IFO – 13275) and

Staphylococcus aureus (IFO – 12732).

[0033]

The method of the antimicrobial evaluation test was as follows : first 4000 μ g / mL suspension of the antimicrobial agent specimen was prepared with sterilized water, and then series of 2 time diluted solutions were prepared by adding sterilized water thereto. Next, 10 % by wt of the above - mentioned series of the diluted solutions was added to a culture medium for sensitivity test that had been sterilized and kept at a temperature of 50 to 60 °C (Mueller Hinton medium (Difco)), and after sufficiently mixing it, it was poured into shallow dishes, followed by solidifying. They were used as flat plates for sensitivity measurement. In addition, Microorganism solutions for inoculation of the above - mentioned test microorganisms were prepared as follows: culture media for multiplication (Mueller Hinton broth (Difco)) were inoculated with respective successively cultured test microorganisms and after culturing then at a temperature of 35 °C for 20 hrs, they were diluted with the culture medium for multiplication so that the number of the

microorganisms might become 10^5 / mL, and they were used as microorganism solutions for inoculation. Next, the above - mentioned flat plates for sensitivity measurement were coated with the microorganism solutions in lines of about 1 to 2 cm by use of a nichrome wire loop (inner diameter, about 1 mm), followed by cultivating at 35 ° C for 35 hrs, and the minimum concentration at which the growth was inhibited was defined to be MIC of the antimicrobial agent. The results of measurements of MIC values by using the respective antimicrobial agents are given in Table 2.

[0034]

Table 2

	MIC value (μ g / mL)		
	E. coli	Pseudonomous aeruginosa	Stapholococcus aureus
Example 1	63	250	125
Example 2	125	250	250
Example 3	250	500	500

Example 4	125	250	250
Example 5	250	500	500
Example 6	250	500	250
Example 7	1000	2000	2000
Example 8	1000	2000	2000
Example for comparison 1	4000	-	-

[0035]

<Antimicrobial evaluation test 2>

By using the antimicrobial agents obtained in Example 1, Example 4 and Example 7 and Example for Comparison 2, evaluation was made on the lasting effects of antimicrobial activities of the antimicrobial agents. The method of the antimicrobial evaluation test was as follows : 1 % suspensions of the respective antimicrobial agent specimens were prepared by use of sterilized water, and after agitating them for pre-

determined periods of time (1, 2 and 4 weeks) by use of a thermostatic agitator kept at 30 °C, filtration and drying thereof were carried out, thereby preparing test specimen samples. Next, by using these test specimen samples, the MIC values for *Escherichia coli* (test microorganism) were measured by the operations similar to Example 1, thereby evaluating the lasting properties of the antimicrobial activities. Here in the case of the antimicrobial agent of Example for Comparison 2, as it was difficult to filter the above - mentioned suspension, it was separated by means of a centrifugal separator (no. of revolutions : 10000 rpm or higher) and the precipitate was dried. The sample thus obtained was used as a test sample. The results of the evaluation of the lasting property of the antimicrobial activities (MIC value) are given in Table 3.

[0036]

Table 3

	MIC value (μ g / mL)			
	0 week	1 week	2 weeks	4 weeks
Example 1	63	63	125	125

Example 4	125	125	125	125
Example 7	1000	1000	1000	1000
Example for comparison 2	63	4000	-	-

[0037]

[Effects of the Invention]

The antimicrobial agents in accordance with the present invention are excellent in compatibility with various types of polymer substrates because an acryl polymer is a carrier for antimicrobial metal and also it is excellent in dispersability for they are of a fine granular form. In addition, with the antimicrobial agents, as the antimicrobial metal is uniformly distributed in the inside of a polymer carrier, the antimicrobial metal is gradually released from the carrier and as a result, they are characterized in that the antimicrobial activities thereof can last for a long period of time. In addition, since the process for the production of the antimicrobial agent in accordance with the present invention is excellent in carrying

effect on a polymer carrier at the time of production in comparison with the emulsion polymerization process that has been known for some times, this process is superior in economy in a case in which an expensive silver salt, etc. are used as an antimicrobial metal.

Continued from the front page

(72) Inventor : Sachihiko Yoshimi

4 – 16- 4, Azuma, Tsukuba City, Ibaraki Prefecture

(72) Inventor : Noriko Itsutsu

2 – 20, Umezono, 2 – chome, Tsukuba City, Ibaraki
Prefecture

THIS PAGE BLANK (USPTO)